(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 413 616 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **90400897.6**

(22) Date of filing: **02.04.90**

(51) Int. Cl.5: **C11D 17/00**, C11D 3/37, C11D 17/08, C11D 1/66

(30) Priority: **18.08.89 US 395856**

(43) Date of publication of application: **20.02.91 Bulletin 91/08**

(84) Designated Contracting States: **BE DE FR GB IT LU SE**

(71) Applicant: **Colgate-Palmolive Company**
300 Park Avenue
New York, N.Y. 10022-7499(US)

(72) Inventor: **Antheunis, Nicole**
Cleyhenslaan 194
B-2850 Keerbergen(BE)
Inventor: **Toussaint, Christine**
Rue de Hermee, 15
B-4480 Oupeye(BE)

(74) Representative: **Le Guen, Gérard et al**
CABINET LAVOIX 2, place d'Estienne d'Orves
F-75441 Paris Cédex 09(FR)

(54) Non-aqueous, nonionic heavy duty laundry detergent.

(57) Stable, Nonaqueous built detergent compositions are provided. The compositions comprise a liquid phase of non-ionic surfactant and a solid, dispersed phase of insolubles at least one of which is a builder such as sodium tripolyphosphate and trisodium citrate. The compositions may also contain bleach, and the conventional adjuvants. Stability and improved dispersibility in water is provided by a carboxy-containing polymer.

EP 0 413 616 A1

BACKGROUND OF THE INVENTION

(1) Field of Invention

This invention relates to stabilization of non-aqueous liquid suspensions, especially non-aqueous liquid fabric-treating compositions. More particularly, this invention relates to non-aqueous liquid laundry detergent compositions which are made stable against phase separation under both static and dynamic conditions and are easily pourable, to the method of preparing these compositions and to the use of these compositions for cleaning soiled fabrics.

(2) Discussion of Prior Art

Liquid nonaqueous heavy duty laundry detergent compositions are well known in the art. For instance, compositions of this type may comprise a liquid nonionic surfactant in which are dispersed particles of a builder, as shown for instance in U.S. Patents No. 4,316,812; 3,630,929; 4,264,466; and 4,661,280.

Liquid detergents are often considered to be more convenient to employ than dry powdered or particulate products and, therefore, have found substantial favor with consumers. They are readily measurable, speedily dissolved in the wash water, capable of being easily applied in concentrated solutions or dispersions to soiled areas on garments to be laundered and are non-dusting, and they usually occupy less storage space. Additionally, the liquid detergents may have incorporated in their formulations materials which can not stand drying operations without deterioration, which materials are often desirably employed in the manufacture of particulate detergent products.

Although they are possessed of many advantages over unitary or particulate solid products, liquid detergents often have certain inherent disadvantages too, which have to be overcome to produce acceptable commercial detergent products. Thus, some such products separate out on storage and others separate out on cooling and are not readily redispersed. In some cases the product viscosity changes and it becomes either too thick to pour or so thin as to appear watery. Some clear products become cloudy and others gell on standing.

The present inventors have been extensively involved as part of an overall corporate research effort in studying the rheological behavior of nonionic liquid surfactant systems with particulate matter suspended therein. Of particular interest have been non-aqueous, built, liquid laundry detergent compositions and the problems of phase separation and settling of the suspended builder and other laundry additives. These considerations have an impact on, for example, product pourability, dispersibility and stability.

It is known that one of the major problems with built, liquid laundry detergents is their physical stability. This problem stems from the fact that the density of the solid suspended particles is higher than the density of the liquid matrix. Therefore, the particles tend to sediment according to stoke's law. No basic solutions exist to solve the sedimentation problem: increasing liquid matrix viscosity and/or reducing solid particle size.

For instance, it is known that such suspensions can be stabilized against settling by adding inorganic or organic thickening agents or dispersants, such as, for example, very high surface area inorganic materials, e.g. finely divided silica, clays etc., organic thickeners, such as the cellulose ethers, acrylic and acrylamide polymers, polyelectrolytes, etc. However, such increases in suspension viscosity are naturally limited by the requirement that the liquid suspension be readily pourable and flowable, even at low temperature. Furthermore, these additives do not contribute to the cleaning performance of the formulation. U.S. Patent 4,661,280 to T. Ouhadi, et al, discloses the use of aluminum stearate for increasing stability of suspensions of builder salts in liquid nonionic surfactant. The addition of small amounts of aluminum stearate increases yield stress without increasing plastic viscosity.

According to U.S. Patent 3,985,668 to W. L. Hartman, an aqueous false body fluid abrasive scouring composition is prepared from an aqueous liquid and an appropriate colloid-forming materials, such as clay or other inorganic or organic thickening or suspending agent, especially smectite clays, and a relatively light, water-insoluble particulate filler material, which, like the abrasive materials, is suspended throughout the false body fluid phase. The lighweight filler has particle size diameters ranging from 1 to 250 microns and a specific gravity less than that of the false body fluid phase. It is suggested by Hartaan that inclusion of the relatively light, insoluble filler in the false body fluid phase helps to minimize phase separation, i.e. minimize formation of a clear liquid layer above the false body abrasive composition, first, by virtue of its buoyancy exerting an upward force on the structure of the colloid-forming agent in the false body phase

counteracting the tendency of the heavy abrasive to compress the false body structure and squeeze out liquid. Second, the filler material acts as a bulking agent replacing a portion of the water which would normally be used in the absence of the filler material, thereby resulting in less-aqueous liquid available to cause clear layer formation and separation.

British Application GB 2,168,377A, published June 18, 1986, discloses aqueous liquid dishwashing detergent compositions with abrasive, colloidal clay thickener and low density particulate filler having particle sizes ranging from about 1 to about 250 microns and densities ranging from about 0.01 to about 0.5 g/cc, used at a level of from about 0.07% to about 1% by weight of the composition. It is suggested that the filler material improves stability by lowering the specific gravity of the clay mass so that it floats in the liquid phase of the composition. The type and amount of filler is selected such that the specific gravity of the final composition is adjusted to match that of the clear fluid (i.e. the compositon without clay or abrasive materials).

It is also known to include an inorganic insoluble thickening agent or dispersant of very high surface area such as finely divided silica of extremely fine particle size (e.g. of 5-100 millimicrons diameter such as sold under the name Aerosil) or the other highly voluminous inorganic carrier materials as disclosed in U.S. Patent 3,630,929.

It has long been known that aqueous swelling colloidal clays, such as bentonite and montmorillonite clays, can be modified by exchange of the metallic cation groups with organic groups, thereby changing the hydrophilic clays to organophilic clays. The use of such organophilic clays as gel-forming clays has been described in U.S. Patent 2,531,427 to E.A. Hauser. Improvements and modifications of the organophilic gel-forming clays are described, for example, in the following U.S. Patents: 2,966,506 - Jordan; 4,105,578 - Finlayson, et al.; 4,208,218 - Finlayson; 4,287,086 - Finlayson; 4,434,075 - Mardis, et al.; 4,434,076 - Mardis, et al.; all assigned to NL Industries, Inc., formerly National Lead Company. According to these NL patents, these organophilic clay gellants are useful in lubricating greases, oil based muds, oil base packer fluids, paints, paint-varnish-lacquer removers, adhesives, sealants, inks, polyester gel coats and the like, However, use as a stabilizer in a non-aqueous liquid detergent composition for laundering fabrics has not been suggested.

On the other hand, the use of clays in combination with quaternary ammonium compounds (often referred to as "QA" compounds) to impart fabric softening benefits to laundering compositions has been described. Por instance, mention can be made of the British Patent Application GB 2,141,152 A, published December 12, 1984, to P. Ramachandran, and the many patents referred to therein for fabric softening compositions based on organophilic QA clays.

According to the aforementioned U.S. Patent 4,264,466 to Carleton, et al., the physical stability of a dispersion of the particulate materials, such as detergent builders, in a non-aquoeus liquid phase is improved by using as a primary suspending agent an impalpable chain structure type clay, including sepiolite, attapulgite, and palygorskite clays. The patentees state the comparative examples in this patent show that other types of clays, such as montmorillonite clay, e.g. Bentolite L. hectorite clay (e.g. Veegum T) and kaolinite clay (e.g. Hydrite PX), even when used in conjunction with an auxiliary suspension aid, including cationic surfactants, inclusive of QA compounds, are only poor suspending agents. Carleton, et al. also refer to use of other clays as suspension aids and mention, as examples, U.S. Patents 4,049,034 and 4,005,027 (both aqueous systems); and U.S. Patents 4,166,039; 3,259,574; 3,557,037 and 3,549,542; and U.K. Patent Application 2,017,072.

Commonly assigned copending application Serial No. 063,199, filed June 12, 1987 (Atty's Docket IR-347LG) discloses incorporation into non-aqueous liquid fabric treating compositions of up to about 1% by weight of an organophilic water-swellable smectite clay modified with a cationic nitrogen-containing compound including at least one long chain hydrocarbon having from about 8 to about 22 carbon atoms to form an elastic network or structure throughout the suspension to increase the yield stress and increase stability of the suspension.

While the addition of the organophilic clay improves stability of the suspension, still further improvements are desired especially for particulate suspensions having relatively low yield values for optimizing dispensing and dispersion during use.

Grinding to reduce the particle size as a means to increase product stability provides the following advantages:

(1) the particle specific surface area is increased, and, therefore, particle wetting by the non-aqueous vehicle (liquid non-ionic) is proportionately improved; and

(2) the average distance between pigment particles is reduced with a proportionate increase in particle-to-particle interaction.

Each of these effects contributes to increase the rest-gel strength and the suspension yield stress while

at the same time grinding significantly reduces plastic viscosity.

The above-mentioned U.S. Patent 4,316,812 discloses the benefits of grinding solid particles, e.g., builder and bleach, to an average particle diameter of less than 10 microns. However, it has been found that merely grinding to such small particle sizes does not, by itselt, impart sufficient long term stability against phase separation.

In the commonly assigned copending application filed on July 15, 1987 in the names of N. Dixit, et al. under Serial No. 073,653 (Attorney's Docket I.R.-4494), and titled "STABLE NON-AQUEOUS CLEANING COMPOSITION CONTAINING LOW DENSITY FILLER AND METHOD OF USE" the use of low density filler material for stabilizing suspensions of finely divided solid particulate matter in a liquid phase against phase separation by equalizing the densities of the dispersed particle phase and the liquid phase is disclosed. These modified liquid suspensions exhibit excellent phase stabilization when left to stand for extended periods of time, e.g., up to 6 months or longer or even when subjected to moderate shaking. However, it has recently been observed that when the low-density filler modified suspensions are subjected to strong vibrations, such as may be encountered during transportation by rail, truck, etc., the homogeneity of the dispersion is degraded as a portion of the low density filler migrates to the upper surface of the liquid suspension.

In commonly assigned, copending application Serial No. 073,551 filed July 15, 1987 in the name of Cao et al. (Attorney's Docket IR 344LG) entitled "Stable Non-Aqueous Suspension Containing Organophilic Clay And Low Density Filler" the use of the low density filler material for stabilizing suspensions of finely divided solid particulate matter in liquid phase against phase separation is disclosed as being improved by the incorporation of organophilic modified clays which aid in resisting the destabilizing effect of strong vibrations.

Nonetheless, still further improvements are desired in the stability of non-aqueous liquid fabric treating compositions.

In addition to the problem of settling or phase separation the non-aqueous liquid laundry detergents based on liquid nonionic surfactants suffer from the drawback that the nonionics tend to gell when added to cold water. This is a particularly important problem in the ordinary use of European household automatic washing machines where the user places the laundry detergent composition in a dispensing unit (e.g. a dispensing drawer) of the machine. During the operation of the machine the detergent in the dispenser is subjected to a stream of cold water to transfer it to the main body of wash solution. Especially during the winter months when the detergent composition and water fed to the dispenser are particularly cold, the detergent viscosity increases markedly and a gel forms. As a result some of the composition is not flushed completely off the dispenser during operation of the machine, and a deposit of the composition builds up with repeated wash cycles, eventually requiring the user to flush the dispenser with hot water.

The gelling phenomenon can also be a problem whenever it is desired to carry out washing using cold water as may be recommended for certain synthetic and delicate fabrics or fabrics which can shrink in warm or hot water.

Partial solutions to the gelling problem in aqueous, substantially builder-free compositions have been proposed and include, for example, diluting the liquid non-ionic with certain viscosity controlling solvents and gel-inhibiting agents, such as lower alkanols, e.g. ethyl alcohol (see U.S. Patent No. 3,953,380), alkali metal formates and adipates (see U.S. Patent No. 4,363,147), hexylene glycol, polyethylene glycol, etc. and nonionic structure modification and organization.

As an example of nonionic surfactant modification one particularly successul result has been achieved by providing an acid group on the nonionic. In this regard see U.S. Patent 4,749,512, the disclosure of which is incorporated herein by reference.

In addition, these two patents each disclosed the use of up to at most about 2.5% of the lower alkyl (C_1 - C_4) etheric derivatives of the lower (C_2 - C_3) polyols, e.g. ethylene glycol, in these aqueous liquid builder-free detergents in place of a portion of the lower alkanol, e.g. ethanol, as a viscosity control solvent. To similar effect are U.S. Patent Nos. 4,111,855 and 4,201,686. However, there is no disclosure or suggestions in any of these patents that these compounds, some of which are commercially available under the tradename Cellosolve R , could function effectively as viscosity control and gel-preventing agents for non-aqueous liquid nonionic surfactant compositions, especially such compositions containing suspended builder salts, such as the polyphosphate compounds or alkali metal citrate,and especially particularly such compositons which do not depend on or require the lower alkanol solvents as viscosity control agents.

Furthermore, British Patent Specification No. 1,600,981 mentions that in non-aqueous nonionic detergent compositions containing builders suspended therein with the aid of certain dispersants for the builder, such as finely divided silica and/or polyether group containing compounds having molecular weights of at least 500, it may be advantageous to use mixtures of nonionic surfactants, one of which fulfills a surfactant

function and the other of which both fulfills a surfactant function and reduces the pour point of the compositions. The former is exemplified by C_{12} - C_{15} fatty alcohols with 5 to 15 moles of etylene and/or propylene oxide per mole.

The other surfactant is exemplified by linear C_6 - C_8 or branched C_8 - C_{11} fatty alcohols with 2 to 8 moles ethylene and/or propylene oxide per mole. Again, there is no teaching that these low carbon chain compounds could control the viscosity and prevent gelation of the heavy duty non-aqueous liquid nonionic surfactant compositions with builder suspended in the nonionic liquid surfactant.

Summary of the Invention

Accordingly, it is an object of this invention to provide liquid fabric treating compositions which are suspensions of insoluble fabric-treating particles in a non-aqueous liquid and which are storage and transportation stable, easily pourable and dispersible in cold, warm or hot water.

Another object of this invention is to formulate highly built heavy duty non-aqueous liquid nonionic surfactant laundry detergent compositions which resist settling of the suspended solid particles or separation of the liquid phase.

A still further object of this invention is to provide nonionic liquids compositions which are readily dispersible in water, particularly laundry bath water.

The foregoing objects are achieved by providing a heterogenous system of solids in a liquid medium which is structured to act as a solid during states of rest and under the ordinary stresses of vibrations, oscillations, shear forces and the like which occur during the handling (e.g. transportation etc.) of the packaged product. When the structure is broken or destroyed, the system acts as a conventional solids suspension in a liquid vehicle or matrix, i.e. it is flowable, pourable, and of course in this state, Stokes Law takes over and the solid suspended matter may settle and the liquid solid phases stratify. It has been determined that several rheological parameters are meaningful indications ofthe stability of a solids suspension in a liquid phase system. Some of these parameters are storage modulus or loss modulus (G''), relaxation time, critical strain (i.e. structure not destroyed below the strain), and structure recovery. Targets to reach for optimized stability are a long relaxation time ($G'>G''$), a critical strain above 0.1 and a recovery time shorter than 1 minute.

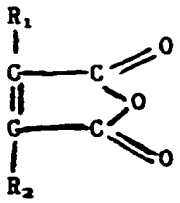
These and other objects of the invention which will become more apparent hereinafter have been accomplished based on the inventors' discovery that by adding a relatively small amount of an amphiphilic carboxy-containing addition polymer. The polymers are derived from α, β-monethylenically unsaturated carboxy-containing monomers which also contain at least one other chalcogen-containing group substituted with at least one group of at least 2 carbon atoms.

The polymers may be homopolymers, copolymers, ter-polymers (i.e. interpolymers) or block interpolymers (e.g. block copolymers).

The polymers may vary in molecular weight from several (2, 3, 4 etc.) hundred, preferably several thousand (2, 3, 4, 5 etc.) and more preferably tens of thousands (e.g. 20,000, 30,000, 50,000, 70,000) to several million (2, 3, 8, 10 etc.). The most highly preferred ranges will depend somewhat on the particularly monomer moieties, but generally this will be about MW = 75,000 to 750,000. The amount of polymer in the composition may vary from about 0.01% to about 10% by weight, and preferably from about 0.05% to about 5% by weight. Typical amounts are 0.10; 0.20 and 0.25.

The polymer, in addition to the carboxy group contains (preferably in the same monomer moiety) a further chalecogen group, i.e. oxygen, nitrogen or sulfur, which is substituted by a grouping of at least 2 carbon atoms. Illustrative groups are carboxy, carboxamido, sulfonate, etc. Specific groups include carboethoxy, carbobutoxy, N-ethyl carboxamido, N,N-diethyl carboxamido, N-n-butyl-carboxamido, etc.

Specific monomer moieties of particular advantage are the α, β-unsaturated dicarboxylic anhydride and especially those of the formula



wherein R_1 and R_2 are independently selected from the group consisting of hydrogen, halogen, alkyl, aryl, aralkyl, (and substituted alkyl, aryl or aralkyl), or $-SO_3H$.

Example of these compounds are:
maleic anhydride
chloromaleic anhydride
citraconic anhydride (methylmaleic)
fumaric anhydride
mesaconic anhydride
phenylmaleic anhydride
benzyl maleic anhydride
sulfomaleic anhydride
aconitic anhydride
itaconic anhydride
methylene malonic anhydride
alkyl succinic anhydride and the like

It is preferred to provide the carboxy monomer moieties in conjunction with other copolymerizable α, β-ethylenically unsaturated monomers. These include:
vinyl ethers e.g.,
vinyl methyl ether
vinyl ethyl ether
vinyl n-propyl ether
vinyl iso-proply ether
vinyl n-butyl ether
vinyl iso-butyl ether
vinyl iso-octyl ether
vinyl phenyl ether
a-chlorovinyl phenyl ether
vinyl B-naphthyl ether
vinyl esters, e.g.,
vinyl acetate
vinyl propionate
vinyl butyrate
vinyl caproate
vinyl stearate, etc.
vinyl halides, e.g.,
vinyl chloride
vinyl fluoride
vinyl bromide
acrylic acid and esters, e.g.,
methyl acrylate
ethyl acrylate
propyl acrylate
acrylic acid derivatives, e.g.,
methacrylic acid and esters
a-haloacrylic acid and esters
acrylonitrile
methacrylonitrile
acrylamide
methacrylamide
N-alkyl acrylamides
N-aryl acrylamides
N-vinyl heterocycles, e.g.,
N-vinyl pyrrolidone
N-vinyl 3-morpholinones
N-vinyl oxazolidone
N-vinyl imidazole
styrene

alkyl styrenes, e.g., a-methyl styrene
vinylidene chloride
vinyl ketones, e.g., methyl vinyl ketone
olefins such as
ethylene
propylene
isobutylene
butene-1
2,4,4-trimethyl pentene-1
hexene-1
3-methyl-butene-1, and the like.

The anhydride-ethylenically unsaturated interpolymers preferably contain the two moieties in equimolar amount whereby the repeating unit in the interpolymer contains 1 anhydride and 1 comonomer moiety. Other ratios are feasible 3.t. 5:4, 4:5, 3:2, 2:3, 2:1, 1:2 etc.

Examples of specific interpolymers which may be employed are:
vinyl methyl ether-maleic anhydride
vinyl ethyl ether-maleic anhydride
styrene-maleic anhydride
a-methyl styrene-maleic anhydride
ethylene-maleic anhydride
vinyl methyl ether-citraconic anhydride
vinyl methyl ether-itaconic anhydride
vinyl methyl ether-chlormaleic anhydride
vinyl chloride-maleic anhydride
vinyl acetate-maleic anhydride
vinyl chloride-vinyl acetate-maleic anhydride
styrene-vinyl acetate-maleic anhydride

An especially useful type of polymer (Z) is one based on an α, β-ethylenically-unsaturated dicarboxylic acid or anhydride (e.g. maleic anhydride) and a copolymerizable α, β- ethylenically unsaturated comoner (e.g. vinyl methylether, ethylene, styrene, N-vinyl pyrrolidone etc.). A further particularly useful sub-group covers the mono esters (e.g. 1/2-butyl, 1/2-ethyl, 1/2-isohexyl) of these polymers. Another useful subgroup involves the cross-linked (or reaction products) of the interpolymers and especially polymers of the Z type utilizing a difunctional reagent such as a diol, di-theol or the like. Illustrative crosslinking atents are glycols such as diethylene glycol, triethylene glycol, 1,6 hexanediol, polyethylene glycols with molecular weights ranging from several hundred (e.g. 200, 300, 400, etc.) to several hundred thousand (100,000; 150,000; 200,000; 250,000; 350,000; 500,00 etc.) and especially those in the range of about 400 to about 40,000. Where such a cross linking agent is used, the amount thereof may vary from 1% by height based on the weight of the polymer to 10 times the weight of the polymer, preferably the ratio of polymer to cross-linker should range from about 10:1 to 1:5 and most preferably 5:1 to 1:2.

In the preferred embodiment of special interest herein the liquid phase of the composition of this invention is comprised predominantly or totally of liquid nonionic synthetic organic detergent. A portion of the liquid phase may be composed, however, of organic solvents which may enter the composition as solvent, vehicles or carriers for one or more of the solid particulate ingredients, such as in enzyme slurries, perfumes, and the like. Also as will be described in detail below, organic solvents, such as alcohols and ethers, may be added as further viscosity control and anti-gelling agents.

The nonionic synthetic organic detergents employed in the practice of the invention may be any of a wide variety of such compounds, which are well known and, for example, are described at length in the text Surface Active Agents , Vol. II, by Schwartz, Perry and Berch, published in 1958 by Interscience Publishers, and in McCutcheon's Detergents and Emulsifiers , 1969 Annual, the relevant disclosures of which are hereby incorporated by reference. Usually, the nonionic detergents are poly-lower alkoxylated lipophiles wherein the desired hydrophile-lipophile balance is obtained from addition of a hydrophilic poly-lower alkoxy group to a lipophilic moiety. A preferred class of the nonionic detergent employed is the poly-lower alkoxylated higher alkanol wherein the alkanol is of 10 to 22 carbon atoms and wherein the number of mols of lower alkylene oxide (of 2 or 3 carbon atoms) is from 3 to 20. Of such materials it is preferred to employ those wherein the higher alkanol is a higher fatty alcohol of about 12 to 18 carbon atoms and which contain from 3 to 14, preferably 3 to 12 lower alkoxy groups per mol. The lower alkoxy is often just ethoxy but in some instances, it may be desirably mixed with propoxy, the latter, if present, often being in a minor (less than 50% proportion). Exemplary of such compounds are those wherein the alkanol is of 12 to 15 carbon

atoms and which contain about 7 ethylene oxide groups per mol, e.g., Neodol 25-7 and Neodol 23-6.5, which products are made by Shell Chemical Company, Inc. The former is a condensation product of a mixture of higher fatty alcohols averaging about 12 to 15 carbon atoms, with about 7 mols of ethylene oxide and the latter is a corresponding mixture wherein the carbon atom content of the higher fatty alcohol is 12 to 13 and the number of ethylene oxide groups present averages about 6.5. The higher alcohols are primary alkanols. Other examples of such detergents include Tergitol 15-S-7 and Tergitol 15-S-9, both of which are linear secondary alcohol ethoxylates made by Union Carbide Corp. The former is mixed ethoxylation product of 11 to 15 carbon atoms linear secondary alkanol with seven mols of ethylene oxide and the latter is a similar product but with nine mols of ethylene oxide being reacted.

Also useful in the present compositions as a component of the nonionic detergent are higher molecular weight nonionics, such as Neodol 45-11, which are similar ethylene oxide condensation products of higher fatty alcohols, with the higher fatty alcohol being of 14 to 15 carbon atoms and the number of ethylene oxide groups per mol being about 11. Such products are also made by Shell Chemical Company. Another preferred class of useful nonionics are represented by the commercially well know class of nonionics which are the reaction product of a higher linear alcohol and a mixture of ethylene and propylene oxides, containing a mixed chain of ethylene oxide and propylene oxide, terminated by a hydroxyl group. Examples include the nonionics sold under the Plurafac trademark of BASF, such as Plurafac RA30, Plurafac RA40 (a C_{13}-C_{15} fatty alcohol condensed with 7 moles propylene oxide and 4 moles ethylene oxide), Plurafac D25 (a C_{13}-C_{15} fatty alcohol condensed with 5 moles propylene oxide and 10 moles ethylene oxide), Plurafac B26, and Plurafac RA50 (a mixture of equal parts Plurafac D25 and Plurafac RA40).

Generally, the mixed ethylene oxide-propylene oxide fatty alcohol condensation products represented by the general formula

$RO(C_3H_6O)_p(C_2H_4O)_qH$,

wherein R is a straight or branched primary or secondary aliphatic hydrocarbon, preferably alkyl or alkenyl, especially preferably alkyl, of from 60 to 20, preferably 10 to 18, especially preferably 12 to 18 carbon atoms, p is a number of up to 14, preferably 3 to 8, and q is a number of up to 14, preferably 3 to 12, can be advantageously used where low foaming characteristics are desired. In addition, these surfactants have the advantage of low gelling temperatures.

Another group of liquid nonionics are available from Shell Chemical Company, Inc. under the Dobanol trademark: Dobanol 91-5 is an ethoxylated C_9-C_{11} fatty alcohol with an average of 5 moles ethylene oxide; Dobanol 25-7 is an ethoxylated C_{12}-C_{15} fatty alcohol with an average of 7 moles ethylene oxide; etc.

In the preferred poly-lower alkoxylated higher alkanols, to obtain the best balance of hydrophilic and lipophilic moieties the number of lower alkoxies will usually be from 40% to 100% of the number of carbon atoms in the higher alcohol, such as 40 to 60% thereof and the nonionic detergent will often contain at least 50% of such preferred poly-lower alkoxy higher alkanol.

Higher molecular weight alkanols and various other normally solid nonionic detergents and surface active agents may be contributory to gelation of the liquid detergent and consequently, will preferably be omitted or limited in quantity in the present compositions, although minor proportions thereof may be employed for their cleaning properties, etc. With respect to both preferred and less preferred nonionic detergents the alkyl groups present therein are generally linear although branching may be tolerated, such as at a carbon next to or two carbons removed from the terminal carbon of the straight chain and away from the alkoxy chain, if such branched alkyl is not more than three carbons in length. Normally, the proportion of carbon atoms in such a branched configuration will be minor rarely exceeding 20% of the total carbon atom content of the alkyl. Similarly although linear alkyls which are terminally joined to the alkylene oxide chains are highly preferred and are considered to result in the best combination of detergency, biodegradability and non-gelling characteristics, medial or secondary joinder to the alkylene oxide in the chain may occur. It is usually in only a minor proportion of such alkyls, generally less than 20% but, as is the case of the mentioned Tergitols, may be greater. Also, when propylene oxide is present in the lower alkylene oxide chain, it will usually be less than 20% thereof and preferably less than 10% thereof.

When greater proportions of non-terminally alkoxylated alkanols, propylene oxide-containing poly-lower alkoxylated alkanols and less hydrophile-lipophile balanced nonionic detergent than mentioned above are employed and when other nonionic detergents are used instead of the preferred nonionics recited herein, the product resulting may not have as good detergency, stability, viscosity and non-gelling properties as the preferred compositions but use of viscosity and gel controlling compounds can also improve the properties of the detergents based on such nonionics. In some cases, as when a higher molecular weight poly-lower alkoxylated higher alkanol is employed, often for its detergency, the proportion thereof will be regulated or limited in accordance with the results of routine experiments, to obtain the desired detergency and still have the product non-gelling and of desired viscosity. Also, it has been found that it is only rarely necessary to

utilize the higher molecular weight monionics for their detergent properties since the preferred nonionics described herein are excellent detergents and additionally, permit the atainment of the desired viscosity in the liquid detergent without gelation at low temperatures. Mixtures of two or more of these liquid nonionics can also be used and in some cases advantages can be obtained by the use of such mixtures.

In view of their low gelling temperatures and low pour points, another preferred class of nonionic surfactants includes the C_{12}-C_{13} secondary fatty alcohols with relatively narrow contents of ethylene oxide in the range of from about 7 to 9 moles, especially about 8 moles ethylene oxide per molecule and the C_9-C_{11}, especially C_{10} fatty alcohols ethoxylated with about 6 moles ethylene oxide.

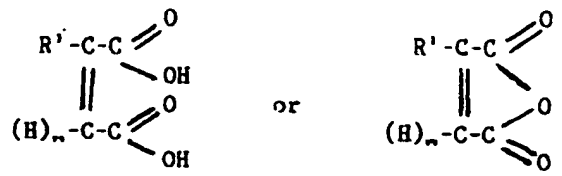
Furthermore, in the compositions of this invention, it may be advantageous to include an organic solvent or diluent which can function as a viscosity control and gel-inhibiting agent for the liquid nonionic surface active agents. Lower (C_1-C_6) aliphatic alcohols and glycols, such as ethonol, isopropanol, ethylene glycol, hexylene glycol and the like have been used for this purpose. Polyethylene glycols, such as PEG 400, are also useful diluients. Alkylene glycol ethers, such as the compounds sold under the trademarks, Carbopol and Carbitol which have relatively short hydrocarbon chain lengths (C_2-C_8) and a low content of ethylene oxide (about 2 to 6 EO units per molecule) are especially useful viscosity control and anti-gelling solvents in the compositions of this invention. This use of the alkylene glycol ethers is disclosed in U.S. Patent No. 4,753,750 filed December 31, 1984, to T. Ouhadi, et al. the disclosure of which is incorporated herein by reference. Suitable glycol ethers can be represented by the following general formula $RO(CH_2CH_2CH_2O)_nH$ where R is a C_2-C_8, preferably C_2-C_8 alkyl group, and n is a number of from about 1 to 6, preferably 1 to 4, on average.

Specific examples of suitable solvents include ethylene glycol monoethyl ether (C_2H_5-O-CH_2CH_2OH), diethylene glycol monobutyl ether (C_4H_9-O-$(CH_2CH_2O)_2H$), tetraethylene glycol monooctyl ether (C_8H_{17}-O-$(CH_2CG_2O)_4H$), etc. Diethylene glycol monobutyl ether is especially preferred.

Another useful antigelling agent which can be included as a minor component of the liquid phase, is an aliphatic linear or aliphatic monocyclic dicarboxylic acid, such as the C_6 to C_{12} alkyl and alkenyl derivatives of succinic acid or maleic acid, and the corresponding anhydrides or an aliphatic monocyclic dicarboxylic acid compound. The use of these compounds as antigelling agents in non-aqueous liquid heavy duty built laundry detergent compositions is disclosed in U.S. Patent No. 4,744,916 to Adams & Prossin filed July 18, 1985, the disclosure of which is incorporated herein in its entirety by reference thereto.

Briefly, these gel-inhibiting compounds are aliphatic linear or aliphatic monocyclic dicarboxylic acid compounds. The aliphatic portion of the molecule may be saturated or ethylenically unsaturated and the aliphatic linear portion may be straight of branched. The aliphatic monocylic molecules may be saturated or may include a single double bond in the ring. Furthermore, the aliphatic hydrocarbon ring may have 5- or 6-carbon atom in the ring, i.e. cyclopentyl, cyclopentenyl, cyclohexyl, or cyclohexenyl, with one carboxyl group bonded directly to a carbon atom in the ring and the other carboxyl group bonded to the ring through a linear alkyl or alkenyl group.

The aliphatic linear dicarboxylic acids have at least about 6 carbon atoms in the aliphatic moiety and may be alkyl or alkenyl having up to about 14 carbon atoms, with a preferred range being from about 8 to 13 carbon atoms, especially preferably 9 to 12 carbon atoms. One of the carboxylic acid groups (-COOH) is preferably bonded to the terminal (alpha) carbon atom of the aliphatic chain and the other carboxyl group is preferably bonded to the next adjacent (beta) carbon atom or it may be spaced two or three carbon atoms from the -position, i.e. on the γ or δ carbon atoms. The preferred aliphatic dicarboxylic acids are the α,β-dicarboxylic acids and the corresponding anhydrides, and especially preferred are derivatives of succinic acid of maleic acid and have the general formula:

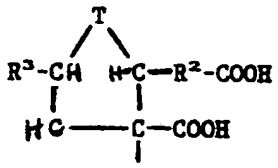


wherein R' is an alkyl or alkenyl group of from about 6 to 12 carbon atoms, preferably 7 to 11 carbon atoms, especially preferably 8 to 10 carbon atoms, wherein $_n=1$, when —is a double bond and $_n=2$, when —is a single bond.

The alkyl or alkenyl group may be straight or branched. The straight chain alkenyl groups are especially preferred. It is not necessary that R' represent a single alkyl or alkenyl group and mixtures of

different carbon chain lengths may be present depending on the starting materials for preparing the dicarboxylic acid.

The aliphatic monocyclic dicarboxylic acid may be either 5- or 6-membered carbon rings with one or two linear aliphatic groups bonded to ring carbon atoms. The linear aliphatic groups should have at least about 6, preferably at least about 8, especially preferably at least about 10 carbon atoms, in total, and up to about 22, preferably up to about 18, especially preferably up to about 15 carbon atoms. When two aliphatic carbon atoms are present attached to the aliphatic ring they are preferably located para- to each other. Thus, the preferred aliphatic cyclic dicarboxylic acid compounds may be represented by the following structural formula



where -T- represents $-CH_2-$, $-CH_2=$, $-CH_2-CH_2-$ or $-CH=CH-$;
R_2 represents an alkyl or alkenyl group of from 3 to 12 carbon atoms; and
R_3 represents a hydrogen atom or an alkyl or alkenyl group of from 1 to 12 carbon atoms,
with the proviso that the total number of carbon atoms in R^2 and R^3 is from about 6 to about 22.

Preferably -T- represents $-CH_2-CH_2-$ or $-CH=CH-$, especially preferably $-CH=CH-$.

R^2 and R^3 are each preferably alkyl groups of from about 3 to about 10 carbon atoms, especially from about 4 to about 9 carbon atoms, with the total number of carbon atoms in R^2 and R^3 being from about 8 to about 15. The alkyl or alkenyl groups may be straight of branched but are preferably straight chains.

The amount of the nonionic surfactant is generally within the range of from about 20 to about 70%, such as about 22 to 60% for example 25%, 30%, 35% or 40% by weight of the composition. The amount of solvent or diluent when present is usually up to 20%, preferably up to 15%, for example, 0.5 to 15%, preferably 5.0 to 12%. The weight ratio of nonionic surfactant to alkylene glycol ether as the viscosity control and anti-gelling agent, when the latter is present, is in the range of from about 100:1 to 1:1, preferably from about 50:1 to about 2:1, such as 10:1, 8:1, 6:1, 4:1 or 3:1. Accordingly, the continuous non-aqueous liquid phase may comprise from about 30% to about 70% by weight of the composition, preferably from about 50% to about 60%.

The amount of the dicarboxylic acid gel-inhibiting compound, when used, will be dependent on such factors as the nature of the liquid nonionic surfactant, e.g. its gelling temperature, the nature of the dicarboxylic acid, other ingredients in the composition which might influence gelling temperature, and the intended use (e.g. with hot or cold water, geographical climate, and so on). Generally, it is possible to lower the gelling temperature to no higher than about 3 °C, preferably no higher than about 0 C, with amount of dicarboxylic acid anti-gelling agent in the range of about 1% to about 30%, preferably from about 1.5% to about 15%, by weight, based on the weight of the liquid nonionic surfactant, although in any particular case the optimum amount can be readily determined by routine experimentation.

The invention detergent compositions in the preferred embodiment also include as an essential ingredient water-soluble and/or water-dispersible detergent builder salts. Typical suitable builders include, for example, those disclosed in the aforementioned U.S. Patents 4,316,812, 4,264,466, 3,630,929, and many others. Water-soluble inorganic alkaline builder salts which can be used alone with the detergent compound or in admixture with other builders are alkali metal carbonates, borates, phosphates, polyphosphates, icarbonates, and silicates. (Ammonium or substituted ammonium salts can also be used.) Specific examples of such salts are sodium tripolyphosphate, sodium carbonate, sodium tetraborate, sodium pyrophosphate, potassium pyrophosphate, sodium bicarbonate, potassium tripolyphosphate, sodium hexametaphosphate, sodium sesquicarbonate, sodium mono and diorthophosphate, and potassium bicarbonate. Sodium tripolyphosphate (TPP) is especially preferred where phosphate containing ingredients are not prohibited due to environmental concerns. The alkali metal silicates are useful builder salts which also function to make the composition anticorrosive to washing machine parts. Sodium silicates of Na_2O/SiO_2 ratios of from 1.6/1 to 1/3.2, especially about 1/2 to 1/2.8 are preferred. Potassium silicates of the same ratios can also be used.

Another class of builders are the water-insoluble aliminosilicates, both of the crystalline and amorphous type. Various cystalline zeolites (i.e. aluminosilicates) are described in British Patent 1,504,168, U.S. Patent 4,409,136 and Danadian Patents 1,072,835 and 1,087,477, all of which are hereby incorporated by reference

for such descriptions. An example of amorphous zeolites useful herein can be found in Belgium Patent 835,351 and this patent too is incorporated herein by reference. The zeolites generally have the formula $(M_2O)_x.(Al_2O_3)_y.(SiO_2)_z.WH_2O$ wherein $_x$ is 1, $_y$ is from 0.8 to 1.2 and preferably 1, $_z$ is from 1.5 to 3.5 or higher and preferably 2 to 3 and W is from 0 to 9, preferably 2.5 to 6 and M is preferably sodium. A typical zeolite is type A or similar structure, with type 4A particularly preferred. The preferred aluminosilicates have calcium ion exchange capacities of about 200 milliequivalents per gram or greater, e.g. 400 meg/o g.

Examples of organic alkaline sequestrant builder salts which can be used alone with the detergent or in admixture with other organic and inorganic builders are alkali metal, ammonium or substituted ammonium, aminopolycarboxylates, e.g. sodium and potassium ethylene diaminetetraacetate (EDTA), sodium and potassium nitrilotriacetates (NTA) and triethanolammonium N-(2-hydroxyethyl)nitrilodiacetates. Mixed salts of these polycarboxylates are also suitable.

Other suitable builders of the organic type include carboxymethylsuccinates, tartronates and glycollates and the polyacetal carboxylates. The polyacetal carboxylates and their use in detergent compositions are described in 4,144,226; 4,315,092 and 4,146,494. Other patents on similar builders include 4,141,676; 4,169,934; 4,201,858; 4,204,852; 4,224,420; 4,225,685; 4,226,960; 4,233,422; 4,233,423; 4,302,564 and 4,303,777. Also relevant are European Patent Application Nos. 0015024, 0021491 and 0063399. Particularly outstanding amoung the organic builders are the non-nitrogeneous polycarboxylates such as citric acid, tartaric acid and the like. The preferred in this group are the sodium and potassium citrates and tartrates and most preferred are the sodium citric acid salts, especially the trisodium citrate, although the monosodium and disodium are also good.

The porportion of the suspended detergent builder, based on the total composition, is usually in the range of from about 30 to 70 weight percent, such as about 20 to 50 weight persent, for example about 40 to 50 weight percent of the composition.

According to the present invention, the physical stability of the suspension of the detergent builder salt or salts or any other finely divided suspended solid particulate additive, such as bleaching agent, pigment, etc., in the liquid vehicle is drastically improved by the presence of small amounts of the amphiphilic polymer.

In preparing the compositions of the present invention, the stabilizer, generally in a flaked or powdered form, is admixed with the other solid ingredients and the liquid components, either in a conventional mixing apparatus, such as a crutcher-type mixer, followed by transfer to a milling apparatus or directly in a milling apparatus. In this latter case, the mill rotor of an Attritor ball mill may be employed to mix the components. In a particularly preferred embodiment of the invention, the stabilizer is first thoroughly mixed with the other solid ingredients, and then this admixture of solid components is mixed with the liquid components.

Since the compositions of this invention are generally highly concentrated, and, therefore, may be used at relatively low dosages, it is often desirable to supplement the builder with an auxiliary builder such as a polymeric carboxylic acid having high calcium binding capacity to inhibit incrustration which would otherwise be caused by formation of an insoluble calcium phosphate, (e.g. where phosphate ion is present as from builder. Such auxiliary builders are also well know in the art. For example, mention can be made Sokolan CP5 which is a copolymer of about equal moles of methacrylic acid and maleic anhydride, completely neutralized to form the sodium salt thereof. The amount of the auxiliary builder is generally up to about 6 weight percent, preferably 1/4 to 4%, such as 1%, 2% or 3%, based on the total weight of the composition.

In addition to the detergent builder, various other detergent additives or adjuvants may be present in the detergent product to give it additional desired properties, either of functional or aesthetic nature. Thus, there may be included in the formulation, minor amount of soil suspending or antiredeposition agents,e.g. polyvinyl alcohol, fatty amides, sodium carboxymethyl cellulose, hydroxy-propyl methyl cellulose, usually in amounts of up to 10 weight percent, for example 0.1 to 10%, preferably 1 to 5%; optical brighteners, e.g. cotton, polyamide and polyester brighteners, for example, stilbene, triazole and benzidone sulfone compositions, especially sulfonated substituted triazinyl stilbene, sulfonated naphthotriazole stilbene benzidine sulfone, et., most preferred are stilbene and triazole combinations. Typically, amount of the optical brightener up to about 2 weight percent, preferably up to 1 weight percent, such as 0.1 to 0.8 weight percent, can be used.

Bluing agents such as utramarine blue; enzymes, preferable prot lytic enzymes, such as subtilisin, bormelin, papain, trypain and pensin, as well as amylasetype enzymes, lipase type enzymes, and mixtures thereof; bactericides, e.g. tetrachlorosalicylanilide, hexachlorophene; fungicides; dyes; pigments (water dispersible); preservatives; ultraviolet absorbers; anti-yellowing agents, such as sodium carboxymethyl cellulose, complex of C_{12} to C_{22} alkyl alcohol with C_{12} to C_{18} alkylsulfate; pH modifiers and pH buffers;

color safe bleaches, perfume, and anti-foam agents or suds-suppressor, e.g. silicon compounds can also be sued.

The bleaching agents are classified broadly for convenience, as chlorine bleaches and oxygen bleaches. Chlorine bleaches are typified by sodium hypochlorite (NaOCl), potassium dichloroiosocyanuate (59% available chlorine), and tricholorisocyanuric acid (95% available chlorine). Oxygen bleaches are preferred and are represented by percompounds which liberate hydrogen peroxide in solution. Preferred examples include sodium and potassium perborates, percarbones, and perphosphate, and potassium monopersulfate. The perborates, particularly sodium perborate monohydrate, are especially preferred.

The peroxygen compound is preferably used in admixture with an activator therefor. Suitable activators which can lower the effective operating temperature of the peroxide bleaching agent are disclosed, for example, in U.S. Patent 4,264,466 or in column 1 of U.S. Patent 4,430.244, the relevant disclosures of which are incorporated herein by reference. Polyacylated compounds are preferred activators; among these, compounds such as tetraacetyl ethylene diamine ("TAED") and pentaacetyl glucose are particularly preferred.

Other useful activators include, for example, acetylsalicylic acid derivatives, ethylidene benzoate acetate and its salts, ethylidene carboxylate acetate and its salts, alkyl and alkenyl succinic anhydride, tetraacetyl-glycouril ("TAGU"), and the derivatives of these. Other useful classes of activators are disclosed, for example, in U.S. Patents 4,111,826, 4,422,950 and 3,661,789.

The bleach activator usually interacts with the peroxygen compound to form a peroxyacid bleaching agent in the wash water. It is preferred to include a sequestering agent of high complexing power to inhibit any undesired reaction between such peroxyacid and hydrogen peroxide in the wash solution in the presence of metal ions. Preferred sequestering agents are able to form a complex with Cu2+ ions, such that the stability constant (pk) of the complexation is equal to or greater than 6, 25° C, in water, of an ionic strength of 0.1 mole/liter, pK being conventionally defined by the formula: pK = -log K where K represents the equilibrium constant. Thus, for example, the pK values for complexation of copper ion with NTA and EDTA at the stated conditions are 12.7 and 18.8, respectively. Suitable sequestering agents include, for example, in addition to those mentioned above, the compounds sold under the Dequest trademark, such as, for example, diethylene triamine pentaacetic acid (DETPA); diethylene triamine pentamethylene phosphoric acid (DTPMP); and ethylene diamine tetramethylene phosphoric acid (EDITEMPA).

In order to avoid loss of peroxide bleaching, e.g. sodium perborate, resulting from enzyme-induced decomposition, such as by catalase enzyme, the compositions may additionally include an enzyme inhibitor compound, i.e. a compound capable of inhibiting enzyme-induced decomposition of the peroxide bleaching agent. Suitable inhibitor compounds are disclosed in U.S. Patent 3,606,990, the relevant disclosure of which is incorporated herein by reference.

Of special interest as the inhibitor compound, mention can be made of hydroxylamine sulfate and other water-soluble hydroxylamine salts. In the preferred nonaqueous compositions of this invention, suitable amounts of the hydroxylamine salt inhibitors can be as low as about 0.01 to 0.4%. Generally, however, suitable amounts of enzyme inhibitors are up to about 15%, for example, 0.1 to 10%, by weight of the composition.

Another useful stabilizer for use where desired in conjunction with the polymer stabilizer, is an acidic organic phosphorus compound having an acidic-POH group, as disicosed in the commonly assigned copending application Serial No. 781,189, filed September 25, 1985, to Broze, et al., acidic organic phosphorus compound, may be, for instance, a partial ester of phosphoric acid and an alcohol, such as an alkanol having a lipophilic character, having, for instance, more than 5 carbon atoms, e.g. 8 to 20 carbon atoms. A specific example is a partial ester of phosphoric acid and a C_{16} to C_{18} alkanol. Empiphos 5632 from Marchon is made up of about 35% monoester and 65% diester. When used amounts of the phosphoric acid compound up to about 3%, preferably up to 1%, are sufficient.

As disclosed in U.S. Patent 4,749,512, to Broze, et al., the disclosure of which is incorporated herein by reference, a nonionic surfactant which has been modified to convert a free hydroxyl group to a moiety having a free carboxyl group, such as a partial ester of a nonionic surfactant and a polycarboxylic acid, can be incorporated into the composition to further improve rheological properties. For instance, amounts of the acid-terminated nonionic surfactant of up to 1 per part of the nonionic surfactant, such as 0.1 to 0.8 part, are sufficient.

Suitable ranges of these optional detergent additives are: enzymes - 0 to 2%, especially 0.1 to 1.3%; corrosion inhibitors - about 0 to 40%, and preferably 5 to 30%; anti-foam agents and suds-suppressor - 0 to 15%, preferably 0 to 5%, for example 0.1 to 3%; thickening agent and dispersants - 0 to 15%, for example 0.1 to 10%, preferably 1 to 5%; soil suspending or anti-redeposition agents and anti-yellowing agents - 0 to 10%, preferably 0.5 to 5%; colorants, perfumes, brighteners and bluing agents total weight 0% to about 2%

and preferably 0% to about 1%; pH modifiers and pH buffers - 0 to 5%, preferably 0 to 2%; bleaching agent - 0 to about 40% and preferably 0% to about 25%, for example 2 to 20%; bleach stabilizers and bleach activators 0 to about 15%, preferably 0 to 10%, for example, 0.1 to 8%; enzyme-inhibitors 0 to 15%, for example, 0.01 to 15%, preferably 0.1 to 10%; sequestering agent of high complexing power, in the range of up to about 5%, preferably 1/4 to 3%, such as about 1/2 to 2%. In the selections of the adjuvants, they will be chosen to be compatible with the main constituents of the detergent composition.

In a preferred form of the invention, the mixture of liquid nonionic surfactant and solid ingredients is subjected to grinding, for example, by a san mill or ball mill. Especially useful are the attrition types of mill, such as those sold by Wiener-Amsterdam or Netzsch-Germany, for example, in which the particle sizes of the solid ingredients are reduced to about 1-10 microns, e.g. to an average particle size of 4 to 5 microns or even lower (e.g. 1 micron). Preferably less than about 10%, especially less than about 5 of all the suspended particles have particle sizes greater than 15 microns, preferably 10 microns. In view of increasing costs in energy consumption as particle size decreases it is often preferred that the average particle size be at least 3 microns, especially about 4 microns. Other types of grinding mills, such as toothmill, peg mill and the like, may also be used.

In the grinding operation, it is preferred that the proportion of solid ingredients be high enough (e.g. at least about 40%, such as about 50%) that the solid particles are in contact with each other and are not substantially shielded from one another by the nonionic surfactant liquid. Mills which employ grinding balls. (ball mills) or similar mobile grinding elements have given very good results. Thus, one may use a laboratory batch attritor having 8 mm diameter steatite grinding balls. For larger scale work a continuously operating mill in which there are 1 mm of 1.5 mm diameter grinding balls working in a very small gap betveen a stator and a rotor operating at a relatively high speed (e.g. a CoBall mill) may be employed; when using such a mill, it is desirable to pass the blend of nonionic surfactant and solids first through a mill which does not effect such fine grinding (e.g. a colloid mill) to reduce the particle size to less than 100 microns (e.g. to about 40 microns) prior to the step of grinding to an average particle diameter below about 18 or 15 microns in the continuous ball mill.

Alternatively, the powdery solid particles may be finely ground to the desired size before blending with the liquid matrix, for instance, in a jet-mill.

It is understood that the foregoing detailed description is given merely by way of illustration and that variation may be made therein without departing from the spirit of the invention.

It should also be understood that as used in the specification and in the appended claims the term "non-aqueous" means absence of water, however, small amounts of water, for example up to about 5%, preferably up to about 2%, may be tolerated in the compositions and, therefore, "non-aqueous" compositions can include such small amounts of water, whether added directly or as a carrier or solvent for one of the other ingredients in the composition.

The liquid fabric treating compositions of this invention may be packaged in conventional glass or plastic vessels and also in single use packages, such as the doserrettes and disposable sachet dispensers disclosed in commonly assigned copending application Serial No. 063,199, filed June 12, 1987 (Attorney's Docket IR-347LG), the disclosure of which is incorporated herein by reference thereto.

The invention will now be described by way of the following non-limiting examples in which all proportions and percentages are by weight, unless otherwise indicate. Also, atmospheric pressure is used unless otherwise indicated.

EXAMPLE I

The following composition is prepared

	% Weight
C9-11 fatty alcohol condensed with 5 moles of ethylene oxide	46.95
Tri-enzymes A*	0.55
Perfume	0.50
Sodium Citrate-dehydrate	30.00
Tetra-acetyl ethylene diamine (TAED)	4.00
Sodium perborate monohydrate	13.70
Na maleate - metracrylate copolymer	2.0
Ethylene diamine tetra acetic acid (EDTA)	0.50
Sodium Carboxymethyl cellulose (CMC)	1.0
Titanium dioxide	0.40
Optical brightener (Tinopol ATS-X)	0.30
Mono Butyl ester of poly (vinyl methyl ether/maleic acid)	0.10

*SAVINASE 8.0 SL (NOVO) 36%
ALCALASE 2.5 SL (NOVO) 46%
TERMAMYL 300 SL (NOVO) 18%
vinyl methyl ether/maleic anhydride
molar ration 1:1; M.W. 305,000

The foregoing composition has a pH = 9.5 when 5 g are dissolved in one liter of water (0.5%). The product is exceptionally stable with no separation or settling of solids after more than 2 months.

EXAMPLE II

Example I is repeated varying the nonionic (and citrate content) as follows
(A) 30% (citrate 47%)
(B) 40% (citrate 37%)
(C) 52% (25% citrate)

EXAMPLE III

Example I is repeated except that the nonionic is replaced by the following in separate formulations in the percent indicated in the final formulation

	%
(A) C_{13} - C_{15} fatty alcohol condensed with 7 moles of ethylene oxide and then 4 moles of propylene oxide	46.95
(B) C_{13} - C_{15} fatty alcohol condensed with 4 moles of propylene oxide and then 7 moles of ethylene oxide	46.95
(C) A & B in 1:1 ratio	46.95

EXAMPLE IV

Examples I to III are each repeated in all parts using, first, 0.05% of the polymer ester, then 0.08%,

then 1.2%, then 1.5%.

EXAMPLE V

Each of the foregoing examples and all parts thereof is repeated utilizing instead of the 1/2 butyl ester (MW 305,000), the following

A) 1/2 butyl ester	MW 262,000
B) 1/2 butyl ester	MW 550,000
C) 1/2 N-propyl ester	MW 305,000
D) 1/2 isohexyl ester	MW 240,000
E) 1/2 isooctyl ester	MW 305,000
(F) 1/2 butyl ester of vinyl ethyl ester-maleic anhydride (1:1) interpolymer	MW 325,000

EXAMPLE VI

Each example is again repeated using hower as the interpolymer the following

A) 1/2 butyl ester of vinyl methyl ether-methyl maleic anhydride (1:1)	MW 350,000
B) 1/2 butyl ester of vinyl methyl ether-citriconic anhydrice (1:1)	MW 420,000
C) 1/2 butyl ester of vinyl pyrrolidone-maleic anhydride (1:1)	MW 300,000
D) 1/2 iso-octyl ester of vinyl pyrrolidone-maleic anhydride (1:1)	MW 450,000

EXAMPLE VII

Examples I, II, III, IV are each repeated using in place of the mono (i.e. 1/2)-butyl ester polymer the following (at equal weight amounts)

A) mono butyl ester of ethylene maleic anhydride interpolymer (1:1)	MW 200,000
B) mono butyl ester of styrene maleic anhydride interpolymer (1:1)	MW 350,000
C) mono butyl ester of vinyl acetate maleic anhydride interpolymer (1:1)	MW 305,000
D) mono ethyl ester of butyl acrylate maleic anhydride interpolymer (1:1)	MW 450,000

EXAMPLE VIII

The following composition is prepared

	% Weight
C_9 - C_{11} fatty alcohol condensed with 5 moles ethylene oxide	38.0
Sodium citrate dehydrate	27.8
Sodium perborate monohydrate	14.5
TAED activator	3.7
CMC	1.0
Titanium dioxide	0.4
Optical brightener	0.3
EDTA	0.5
Trienzymes A	0.55
Perfume	0.5
Pluronic L42 Diol	0.05
Vinyl methyl ether-maleic anhydride Polymer (Gantrez AN 119)	0.0
Propylene carbonate	12.6

A product of excellent stability is obtained.

Claims

1. A stable, non aqueous liquid detergent composition comprising a non-ionic surfactant suspended particles including builder, and from about 0.01 to about 10% by weight of the composition an amphiphilic carboxy-containing polymer.
2. A composition as defined in claim 1 wherein the builder is inorganic phosphate.
3. A composition as defined in claim 1 wherein the builder is an organic carboxylate.
4. A composition as defined in claim 3 wherein the organic carboxylate is selected from the group consisting of ethylenediaminetetraacetic acid, nitrilotriacetic acid, citric acid, and tartaric acid.
5. A composition as defined in claim 4 wherein the polymer contains maleic acid or anhydride moieties.
6. A composition as defined in claim 5 wherein the polymer is an α, β -monoethylenically unsaturated monomer - maleic anhydride interpolymer.
7. A composition as defined in claim 6 wherein the non-ionic surfactant comprises from about 20% to about 70% by weight of the composition, the organic builder from about 20% to about 70% by weight of the composition and the polymer is a vinyl C_1 to C_4 alkyl ether-maleic anhydride interpolymer.
8. A composition as defined in claim 7 wherein the polymer is a partial C_1 to C_{16} aliphatic ester.
9. A composition as defined in claim 8 wherein the polymer is a mono butyl ester.
10. A composition as defined in claim 7 including a diol crosslinking agent in a weight ratio of polymer to crosslinking agent of from about 10:1 to 1:5.
11. A composition as defined in claim 10 wherein the crosslinking agent is a polyethylene glycol and the ratio of polymer to the glycol ranges from about 3:1 to 1:1.
12. A composition as defined in claim 8 including a bleaching compound.
13. A composition as defined in claim 12 wherein the bleach is a peroxygen compound.
14. A composition as defined in claim 13 wherein the peroxygen compound is a perborate monohydrate salt.
15. A composition as defined in claim 14 wherein interpolymer is present in an amount of from about 0.5 to 1.5 weight %.
16. A composition as defined in claim 15 including up to 10% enzymes.
17. A composition as defined in claim 16 wherein the enzymes comprises a mixed enzyme system.
18. A composition according to claim 15 wherein the nonionic is an ethylene-propylene oxide condensate with a reactive-hydrogen-containing hydrophobic of at least 8 carbon atoms.
19. A composition according to claim 18 wherein the non-ionic has the molecular configuration of a condensate of a C_9 or greater alcohol with first 7 moles of ethylene oxide and then 4 moles of propylene oxide.
20. A method for laundering clothes which comprises washing the clothes in an aqueous bath containing the composition of claim 1.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90400897.6

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US - A - 4 326 979 (BUS et al.) * Column 2, lines 3-61; column 3, lines 31-45; column 4, lines 8-19; claim 1; examples H,I,Q,S *	1,2,3,7	C 11 D 17/00 C 11 D 3/37 C 11 D 17/08 C 11 D 1/66
A		12,13,14,18	
A	DE - A1 - 3 511 515 (COLGATE) * Claims; example 1 *	1,2,4,12-14,16	
A	DE - A1 - 3 511 517 (COLGATE) * Claims 1,2,4,11; example *	1,2,12-14,16,18	
D,A	US - A - 4 661 280 (T. OUHADI et al.) * Claims 1,6 *	1,2	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 11 D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	11-10-1990	SEIRAFI

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P0401)